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CORRELATION OF ESTER IMPURITIES
WITH COMPOSITE PROPERTIES

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Abstract

The presumed relationship of chemical impurities to final composite properties is the rationale for most chemical characterization studies. This study examines this relationship for PMR-polyimide resin. Ester/acid solutions of one monomer were aged at selected temperatures and chemical changes were monitored spectroscopically. At selected intervals, graphite fiber reinforced composite panels were fabricated. Changes in resin processing characteristics and composite properties were determined. The correlation of these data are discussed as are related characterization studies of PMR-polyimide resin.

1. INTRODUCTION

Problems resulting from chemical impurities or improper formulation of a polymer system are typically evidenced in two areas: variations in processing response of the resin or variations in final properties of the material. Their potential effect on final material properties is of major concern in high performance polymer matrix composites and has been the rationale for many programs addressing the quality assurance of composite materials. However, the correlation of specific chemical impurities with degradation of physical or mechanical properties of composites has seldom been demonstrated in the literature. For PMR-polyimide resin, the correlation of ester impurities with void formation in composite samples has been qualitatively discussed.⁽¹⁾

The polymer employed in this study was the high temperature resistant, addition-type, polyimide resin system (designated PMR for polymerization of monomer reactants) developed at the Lewis Research Center.⁽²⁾ The PMR-polyimide resin

system uses an alcohol solution of three monomer reactants: an ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), and a diester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE). The ester impurities of concern in this study are the tri- and tetraesters formed by further esterification of BTDE during storage in the alcohol solvent. The purpose of this study was to characterize the formation of these ester impurities and to determine their effect on the mechanical properties of composites.

2. EXPERIMENTAL

The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), the 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and the 4,4'-methylenedianiline (MDA) were the highest quality commercially available materials and were used without further purification. Anhydrous, electronic grade methanol and absolute, undenatured ethanol were employed.

The BTDE solutions prepared for this study were typical of bulk working solutions used in routine composite fabrication. The solutions were prepared by refluxing BTDA in alcohol for approximately two hours. The solutions were formulated to give fifty weight percent BTDE at the end of the reaction. Samples were stored in closed plastic containers at ambient temperature (nominally 25°C), 5°C, and -18°C. Loss of solvent during extended periods of storage appeared minimal. Fully formulated resin solutions were prepared by adding NE, MDA and solvent to the BTDE solutions to give fifty weight percent solutions with monomers in the proportion: n moles of BTDE/ $(n+1)$ moles of MDA/2 moles of NE, where $n=2.08$ for PMR-15.

Nuclear magnetic resonance spectral measurements were obtained on a commercial, 60 MHz, continuous wave instrument. Data were referenced to internal tetramethylsilane. Sample solutions were diluted approximately four fold with deuteriochloroform for the measurements. All data were electronically integrated.

Prepreg tapes were made by drum winding and impregnating HTS-2 graphite fiber with PMR-15 monomer solutions to yield prepreg containing nominally 54.5 percent fiber by weight. The prepreg was air dried for one hour at ambient temperature and one hour at 49°C. The prepreg was cut into 7.6 x 20.3 cm plies and stacked unidirectionally, eight plies thick. These stacks were staged at 121°C for three hours under 0.1 psi load. The composites were cured in a matched metal die preheated to 232°C. Following a dwell time of 10 minutes, 500 psi pressure was applied and the temperature increased to 316°C at 5.5°C/min. Pressure and temperature were maintained for 60 minutes. Prior to test specimen preparation, the laminates were post-cured for 16 hours in a 316°C air circulating oven. All laminates were inspected using ultrasonic C-scan. Flexural strength tests and interlaminar shear tests were performed at

ambient temperature and at 316°C as described in Reference 3. Test specimens were cut, in triplicate, from regions near the ends of the laminates as well as near the center.

3. RESULTS AND DISCUSSION

3.1 BACKGROUND

The PMR-polyimide resin system uses the three monomer reactants shown in Figure 1. (Note that the ethylesters are formed when ethanol is used as solvent.) In practice, an alcohol solution of the monomers is used to impregnate reinforcing graphite fibers and most of the solvent is driven off. The impregnated material is then heated to initiate the condensation reactions which give the amide and imide prepolymers (Figure 1). Final cure is carried out under pressure at a temperature adequate to initiate the addition crosslink reaction of the norbornenyl endcaps. The time/temperature sequence developed for staging and curing the resin is predicated on the chemistry shown in Figure 1. Hence, chemical impurities such as the higher esters of BTDE can affect the process because, compared to BTDE, they may react at different rates or to different extents during the standard cure schedules. The overall reaction sequence for forming BTDE and the higher esters is shown in Figure 2.

3.2 ESTER SOLUTION ANALYSIS

Both methanol and ethanol solutions of BTDE were spectroscopically monitored for ester impurity content as a function of solution storage time. The data for the two solvent systems showed the same general trends. Numerical analysis was carried out only on the methanol solution data because the magnetic resonance spectra of the ethylester solutions contained several overlapping resonance peaks which led to a large degree of uncertainty in the integral data. Consequently, all subsequent discussion refers to the methanol/BTDE system.

The increase in higher ester concentration (as indicated by the number

of ester groups per molecule) during storage of the BTDE solutions is shown in Figure 3 for three storage conditions (ambient, 5°C, and -18°C). The normalization of the magnetic resonance integral data and the calculation of the number of ester groups per molecule were performed as described in Reference 1. The ambient temperature data overlay the data reported in Reference 1. Higher ester formation is significantly retarded during 5°C storage and appears to be essentially stopped at -18°C.

The storage temperatures employed in this study were chosen to be typical of refrigeration conditions likely to be encountered during large scale resin production. This range of temperatures, unfortunately, does not provide an ideal basis for a kinetic analysis of the esterification reaction. Rate constants can be determined only from the ambient and 5°C data. Figure 4 shows the first order rate plots for these data. The normalized residual acid concentration, $[A]$, equals $(4\text{-average number of esters per molecule})/2$. The rate constants, k , defined by the slopes of these curves are: $k(\text{ambient}) = 2.8 \times 10^{-2} \text{ month}^{-1}$ and $k(5^\circ\text{C}) = 0.7 \times 10^{-2} \text{ month}^{-1}$. The Arrhenius activation energy, E_a , defined by these rate constants is approximately 26 kcal/mole, and the pre-exponential factor, A , is approximately 10^{11} sec^{-1} . Both E_a and A are typical of a thermally activated, collision controlled reaction in the liquid phase.

3.3 COMPOSITE SAMPLE ANALYSIS

Graphite fiber prepreg and unidirectional composite panels were fabricated from PMR monomer solutions formulated with the aged BTDE. As noted above, analogous results were attained with both methanol and ethanol solvents and only results based on the methanol/BTDE system will be discussed. Composite samples were prepared at one month intervals from the time of solution preparation (two samples at the two month interval were lost due to problems incurred during prepreg

staging). All observations are referenced to a control panel prepared with a fresh resin solution.

Qualitatively, slight variations in resin flow were observed during processing of these samples. The general trend was an increase in resin flow with increasing age of the BTDE employed in the resin formulation. This trend correlates with the increased higher ester content of the aged BTDE solutions. The increased flow can be rationalized in terms of the greater flexibility and lower melt temperature of higher ester monomers or ester terminated oligomers which persist beyond the typical temperature range for imidization of PMR-polyimide. The observed flow (as indicated by the relative weight of resin lost during press cure) ranged from 1 - 2% for the fresh resin solution to nominally 5% for the resin formulated with BTDE aged three months at ambient conditions. Total resin flow is sensitive to time and temperature of prepreg staging as well as impurity concentration and, consequently, some scatter appeared in the flow observations. The general correlation of increased flow with increased ester concentration, however, appears to hold.

Figure 5 shows the results for ultrasonic inspection of panels prepared with fresh and aged BTDE solutions. The sample formulated with fresh BTDE shows uniform high transmission of sound waves. The sample prepared with BTDE aged three months at ambient conditions shows significant attenuation of sound near the panel ends. In the panels formulated with BTDE aged at ambient conditions and at 5°C, the extent of these regions of attenuation appears to correlate with the higher ester content of the BTDE solutions used to prepare the panels. The BTDE stored at -18°C did not show significant higher ester content and the corresponding panels did not show a significant decrease in ultrasonic transmission. Visual inspection (30x) of selected cross-sections in these regions did not detect significant void content except for the samples prepared

with BTDE aged three months which blistered during post-cure. It is assumed, however, that the decrease in ultrasonic transmission does reflect a decrease in the quality of the polymer matrix material. The distribution of the regions of decreased transmission is consistent with the flow pattern expected for the unidirectional orientation of the fiber reinforcements in the closed rectangular mold. This ultrasonic transmission pattern has been noted in previous studies also (4). Surface discoloration (a grainy gold or yellow-brown color) in the regions of poor transmission was observed on samples prepared with BTDE aged three months at ambient conditions and at 5°C, and these samples formed blisters in those same regions when post-cured at 316°C. The formation of blisters is consistent with the mechanistic arguments discussed in Reference 1.

Figure 6 shows the variation of composite flexural strength and interlaminar shear strength (both evaluated at ambient temperature and 316°C) as a function of BTDE solution storage time. These data were not normalized for fiber content. Normalization would not change the trend in the observed properties. The initial strengths exhibited by these test specimens are typical of high quality PMR-15 laminates. These data show negligible change in flexural and shear strengths for samples formulated with BTDE aged up to two months. However, it appears that these composite properties are decreased in samples formulated with BTDE aged for three months. The ambient temperature data in Figure 1 show that there are nominally 2.2 ester groups per molecule after three months storage (compared with 2.0 esters for fresh BTDE). Thus, it appears that significant degradation of average flexural and shear strengths can be observed when nominally 10% of the BTDE has formed higher ester impurities.

Figure 7 shows, graphically, the correlation of ambient temperature flexural strength and higher ester content in PMR-15 composites. A

decrease in flexural strength with increasing ester content is evident. The apparent linear relationship is described by the equation:

$$\text{Strength}(\text{obsv}) = \text{Strength}(\text{max}) + C \times (\% \text{ higher ester})$$

where $\text{Strength}(\text{max}) \approx 240 \text{ ksi}$

C = correlation coefficient (slope of the curve)

$(\% \text{ higher ester}) = 100 (\text{average ester per molecule} - 2)/2$.

The observed value of the correlation coefficient is, $C = -7 \text{ ksi}$. It should be noted that this coefficient applies only to the ambient temperature flexural strength; however, a similar analysis can be conducted for the other properties observed. Based on this analysis, an upper limit of higher ester impurity content can be defined by specifying an acceptable lower limit of the property. In its simplest form, this implicitly requires an assumption that the composite is uniformly degraded by the impurity content. As noted above, the defects resulting from higher ester impurities in PMR-15 are definitely not uniformly distributed. This latter observation is of particular concern because it implies that the final distribution of mobile impurities (such as higher esters) is dependent upon the geometry of the component being formed (to the extent that the geometry affects resin flow during processing). In the worst case, it might be possible to concentrate a relatively small amount of such defects in a critical area of a component and this could obscure the simple correlation discussed above.

3.4 RELATED STUDIES

Extended storage of BTDE solutions is the best documented source for introduction of higher ester impurities into the PMR-15 resin. Other opportunities for formation of ester impurities do occur. Higher ester impurities have been observed by the authors in preliminary analyses of fully formulated PMR-15 solutions which had been heated at 60°C for approximately six hours.

Also, the concentration of ester impurities in fully formulated PMR-15 monomer solutions was monitored⁽⁵⁾ during extended solution storage at ambient temperature, 5°C, and -18°C. Higher ester impurities from BTDE were not observed during storage periods as long as four months. Diester impurities from NE were detected but did not exhibit any adverse effect on composite properties. It has also been reported⁽⁶⁾ that fully formulated PMR-15 prepreg has been stored up to one year in refrigerated conditions with no adverse effect on resin processing or composite properties.

Based on these observations, it appears that higher ester impurities, and the problems associated with their presence, are not typically observed in fully formulated resin solutions. Only when the solutions are handled at elevated temperatures does it appear that the ester impurities may be forming.

4. SUMMARY OF RESULTS AND CONCLUSIONS

The formation of ester impurities in BTDE monomer solutions has been studied and correlated with PMR-15/graphite fiber composite properties. It was determined that:

1. The concentration of higher ester impurities of BTDE increases with time during ambient and 5°C storage of BTDE solutions.
2. Approximately 10% of the residual acid groups in BTDE react to form higher esters after three months storage at ambient conditions.
3. The rate constants for formation of higher esters in BTDE solutions are: $k(\text{ambient}) = 2.8 \times 10^{-7} \text{ month}^{-1}$ and $k(5^\circ\text{C}) = 0.7 \times 10^{-2} \text{ month}^{-1}$, and the associated Arrhenius parameters are approximately: $E_a = 26 \text{ kcal/mole}$ and $A = 10^{11} \text{ sec}^{-1}$.
4. Graphite reinforced PMR-15 composite samples fabricated with BTDE aged three months at ambient and 5°C exhibit a decrease in flexural and interlaminar shear strengths. The decrease correlates with increasing higher ester content.

5. Ultrasonic inspection of panels prepared with BTDE aged at ambient conditions and 5°C exhibited areas of decreased ultrasonic transmission (decreased resin quality) near the panel ends. The extent of these areas increased with increasing higher ester content.

From these results it is concluded that:

1. Nominally 10% higher ester impurity in PMR-15 resin does affect composite properties.
2. The non-uniform distribution of defects resulting from the mobile ester impurities can compound the degradation of properties.
3. While the formation of higher ester impurities can be severe in aged solutions of BTDE, this is typically not the case in fully formulated PMR solutions.
4. Storage of BTDE at -18°C is sufficient to retard formation of higher ester impurities.

5. REFERENCES

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6. BIOGRAPHY

Richard W. Lauver - Dr. Richard W. Lauver has been employed at NASA-Lewis since 1974. He received a B.A. in Chemistry from Knox College and a Ph.D. in Chemistry from the University of Illinois. His current research is in the area of chemical characterization of polymer and composite materials.

Raymond D. Vannucci - Raymond D. Vannucci has been employed at NASA-Lewis since 1965. He received a B.S. in Engineering from Cleveland State University. Presently he is working as a Materials Engineer in the Polymer Matrix Composites Section. His current research involves the fabrication and characterization of polymer composites.

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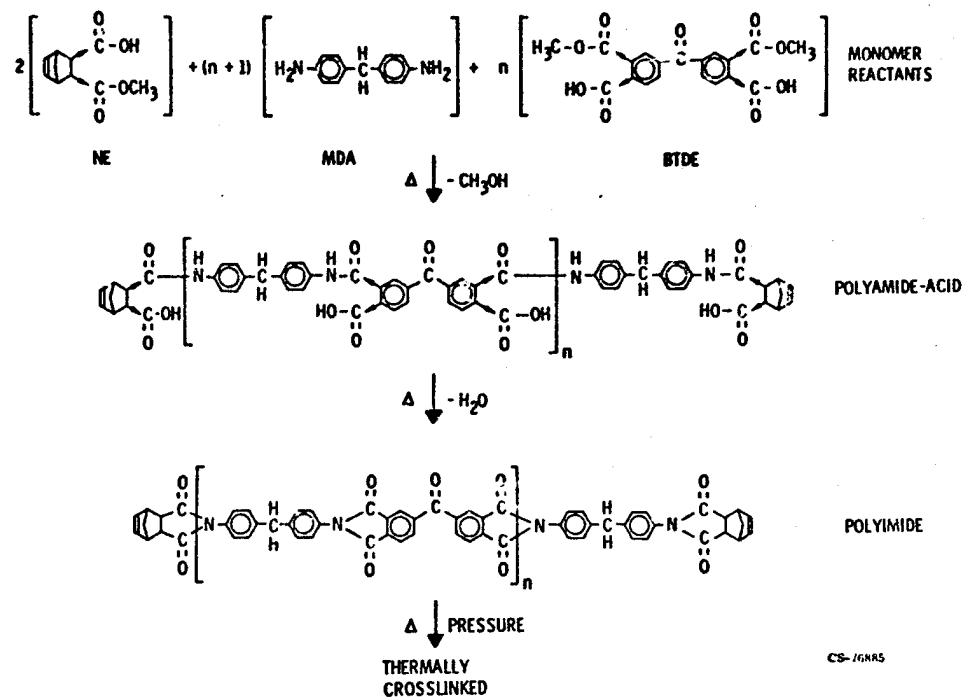


Figure 1. - Reaction sequence for PMR-polyimide resin.

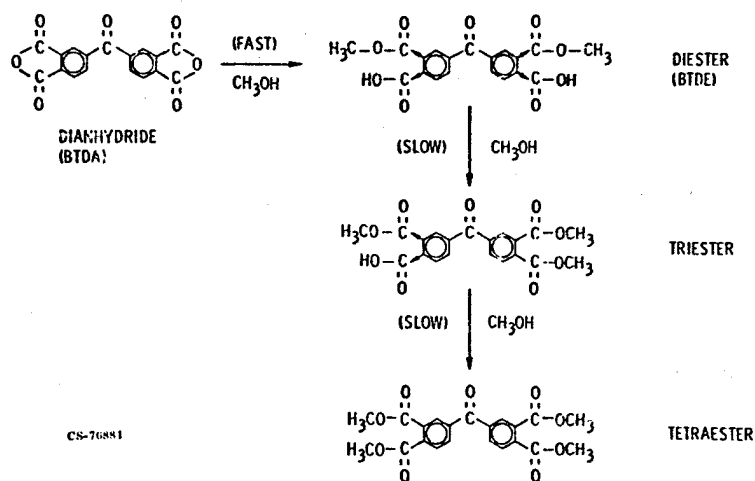


Figure 2. - Reaction sequence for esterification of 3,3',4,4'-benzophenonetetracarboxylic dianhydride.

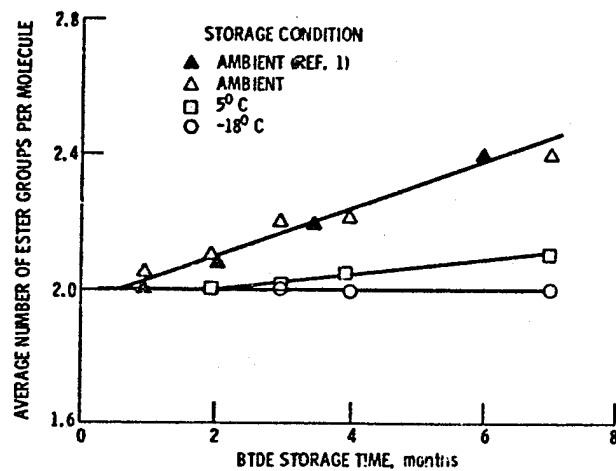


Figure 3. - Increase in number of methylester groups per molecule during storage of 50 weight percent solutions of BTDE.

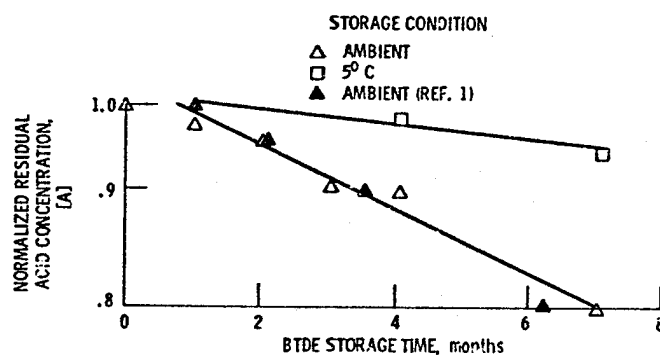


Figure 4. - First order rate plots for higher ester formation in 50 weight percent BTDE during storage.

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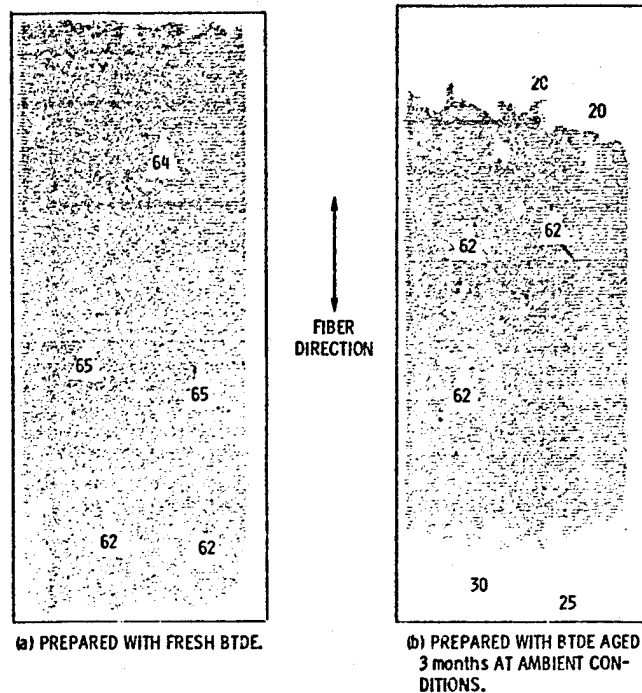


Figure 5. - Ultrasonic C-scans of PMR-15/graphite fiber composites. Dark trace indicates ultrasonic transmission of greater than 50 percent of reference signal. Numbers indicate observed percent transmission at selected areas.

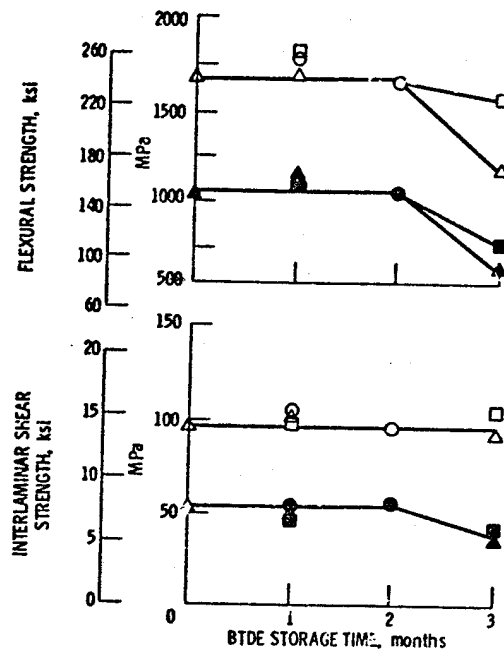


Figure 6. - Variation of flexural strength and interlaminar shear strength in PMR-15 composites fabricated with aged BTDE (Δ ambient storage, \square 5°C storage, \circ -18°C storage; open symbols indicate samples tested at ambient conditions, solid symbols indicate samples tested at 316°C).

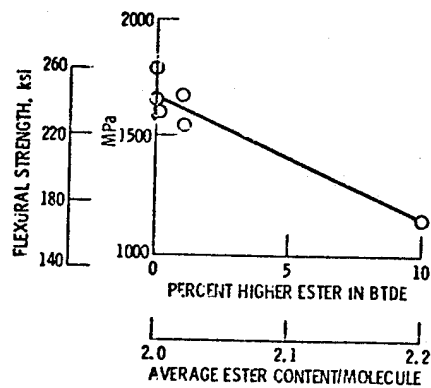


Figure 7. - Correlation of ambient temperature flexural strength with ester impurity content in PMR-15/graphite composites.